## Interstitial water chemistry and nutrients fluxes from tropical intertidal sediment

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Depth profiles of chlorinity, nutrients, pH and alkalinity in interstitial waters from high porosity, carbon rich sediment cores of Gorai creek (near Bombay) were studied in different seasons to evaluate temporal changes in relation to their concentrations in the overlying creek water. The high chlorinity creek water infiltrating in the bed after September, progressively pushed down the monsoonal low chlorinity water trapped in the sediment resulting in a well-defined chlorinity minimum at the intermediate depth which progressively migrated downwards as the dry season advanced. In the presence of high concentrations of NO<sub>3</sub>-N throughout the core lengths, the occurrence of high T<sub>alk</sub> was attributed to the enhanced rate of surface microbial activity and its subsequent downward transport with chlorinity. The inorganic products (NO<sub>3</sub>-N, NO<sub>2</sub>-N, NH<sub>4</sub><sup>+</sup>-N, PO<sub>4</sub><sup>3</sup>-P) of aerobic oxidation of organic matter accumulated in the 0-4 cm sediment section before their transport. The nature of NO<sub>3</sub>-N profile suggested its generation in the surficial sediment followed by utilization in the intermediate level with the consumption rate decreasing in the bottom sections. An intermediate maxima of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3</sup>-P prevailed in most cores which gradually shifted downwards with chlorinity. A continuous build-up of NH<sub>4</sub><sup>+</sup>-N in the interstitial waters unlike other nutrients was evident. Markedly high N:P molar ratios in surficial sections suggested the removal of PO<sub>4</sub><sup>3</sup>-P from interstitial water. The fluxes of all nutrients were oriented towards the water column. Hence, the nutrients released in the surficial interstitial water were partly transported to the overlying water with a significant portion migrating into the sediment with chlorinity.

The diagenetic reactions including adsorption and desorption, mineral formation, diffusion and exchange of solutes and gases within the overlying water, modify the composition of interstitial waters, frequently resulting in steep vertical concentration gradients of several chemical species. Such concentration gradients exhibit pronounced seasonality in the coastal sediment interstitial waters of higher latitudes<sup>1,2</sup> due to temperature dependence of microbial oxidation of the organic matter. However, the information on nearshore tropical sediments where higher ambient temperature accelerates the rate of microbial oxidation and where seasonal changes in temperature are small, is relatively restricted. Hence, diagenesis in the sediment of Gorai creek near Mumbai (Bombay) which receives large fluxes of organic matter was investigated with respect to the sequence of oxidation reactions, and seasonality in behaviour of some chemical species.

## **Materials and Methods**

Gorai creek (Fig. 1) which transects the north-west portion of the suburban Mumbai (Bombay) extends 12 km inland through vast mangrove mudflats and low-lying marshy areas. South of the creek mouth, lies the Akse-Madh coastal strip having a landscape

of fine beaches interrupted occasionally by remnant boulders of headlands. The northern bank of the creek is bordered by Manori village which is relatively less developed and forms a natural beach. The shallow creek is under the high influence of semidiurnal tides with spring and neap ranges of 3.5 m and 1.8 m respectively in the mouth area that induces good tidal flushing of the lower reaches. Though there is no major industrial development in the command area of the creek that can influence the aquatic environment, the point discharges of domestic wastewater in the inner creek exert some influence on water quality. Moreover, the coastal area of Mumbai, particularly the creeks, bays and estuaries receive 1.8 x 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> of largely untreated domestic wastewater apart from industrial effluents<sup>4</sup> roughly put at 0.5 x 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>. These wastewaters eventually drain to the Arabian Sea. The nearshore tidal circulation which is elliptical with an average major axis of 7 km (parallel to the coast), disperses the wastewater constituents widely and hence can influence the environmental quality of Gorai creek<sup>5</sup>, though to a limited extent, in comparison with the nearby Versova and Mahim creeks which are direct recipients of wastes.

Sediment cores up to a length of 52 cm were obtained from the nearshore region of Gorai creek

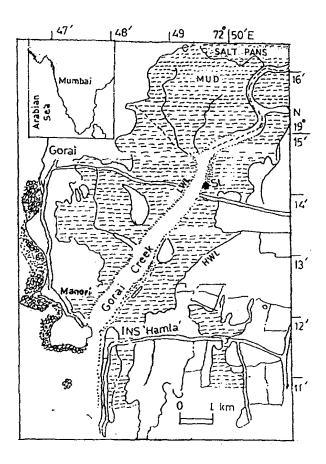


Fig. 1—General map of the area and sampling location (shown as SL in the figure)

(Fig. 1) during low tide by pressing a clean acrylic tube (inner diameter 4.5 cm and outer diameter 5.0 cm) into the bed. The tube was lifted carefully taking utmost care to prevent slipping-out of the sediment. Immediately after retrieval both ends of the tube were sealed with polyethylene caps for transport to the laboratory which was done within 30 min from the time of collection. In order to have sufficient quantity of sediment for extraction, four cores were collected from an area of 1 m<sup>2</sup>, each time. The creek water was also obtained in a precleaned plastic bottle. The sediment cores and creek water were sampled on 12 Aug. 1991 (core 1), 29 Oct. 1991 (core 2), 19 Nov. 1991 (core 3), 3 Jan. 1992 (core 4) and 4 June 1992 (core 5).

Immediately on reaching the laboratory, the sediment was extruded from the tube and sectioned at 4 cm intervals. The sections of all cores of a set at a particular depth were pooled together and transferred to an internally teflon lined stainless steel squeezer resembling the design of Reeburgh sampler<sup>6</sup>. The squeezer was so designed and fabricated that contact

of the sediment with the metal surface was completely avoided. The interstitial water was squeezed out under pressure (10.5 kgF cm<sup>-2</sup>) of instrumental grade (IOLAR-2) nitrogen gas. The time required for collecting 25 ml of interstitial water was 15-20 min. The extracted interstitial water was filtered through a 0.45  $\mu$ m Millipore membrane filter paper fixed in the lower portion of the squeezer itself and collected directly into a precleaned polyethylene bottle. The creek water was also filtered through a 0.45  $\mu$ m Millipore membrane filter paper. These filtrates were analysed for pH, total alkalinity ( $T_{alk}$ ), nitrate ( $NO_3$ -N), nitrite ( $NO_2$ -N), ammonia ( $NH_4$ <sup>+</sup>-N), and phosphate ( $PO_4$ <sup>3</sup>-P) within 1 h of extraction.

The pH was determined with an accuracy of  $\pm 0.02$ pH unit on an ECIL (Electronic Corporation of India Limited) Model 5652 pH meter, using glass-calomel combined electrode. The instrument was calibrated just before use with standard buffer solutions (pH 9.2, 7 and 4). T<sub>alk</sub> (total alkalinity) was estimated by acidimetric titration using pH electrode and graphical determination of the end point<sup>7</sup> and chlorinity by Mohr titration<sup>8</sup>. Standard seawater (Institute of Oceanographic Sciences, U.K.) was used to stan-dardise the silver nitrate solution. The precision of the method was  $\pm 0.2\%$ . NO<sub>3</sub>-N, NO<sub>2</sub>-N, NH<sub>4</sub>+N. and PO<sub>4</sub><sup>3</sup>-P were determined by standard procedures after adequate dilution of interstitial water<sup>9</sup>. The precision of analysis for the respective constituent was  $\pm 2.6\%$ ,  $\pm$  1.8%,  $\pm$  3.2% and  $\pm$  2.9%.

Sediment texture of core 1 was studied by the method of Buchana & Kain  $^{10}$ . Core 2 was analysed for  $C_{\rm org}$  (total organic carbon) and phosphorus ( $P_{\rm total}$ ). For the analysis of  $P_{\rm total}$ , powdered sediment (0.5 g) dried at  $110^{\circ}{\rm C}$  was digested" with concentrated HF, HClO<sub>4</sub> and HNO<sub>3</sub> (10 ml each) in a teflon dish nearly to dryness, the residue was brought into solution in 0.5 M HCl and P was determined by standard procedure  $^{12}$ .  $C_{\rm org}$  was estimated titrimetrically  $^{13}$ . Porosity of core 4 was assessed  $^{14}$  from the loss of weight of the sediment after drying at 60°C.

## **Results and Discussion**

The core 1 of Gorai sediment consisted of silt (41.6-96%) and clay (4.9-57.3%) with a low percentage of sand (1-8%) (Fig. 2). The clay content which plays an important role in early diagenesis was high in the top 20 cm. High sediment porosity (0.77-0.84) was associated with high percentage of fine silt and clay in the sediment 1415 and a marked decrease with

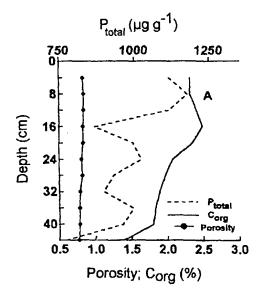
depth (Fig. 2) was largely due to the combined effect of compaction and change in sediment texture<sup>14</sup>. Though the C<sub>org</sub> in the cores varied in a relatively narrow range (1.4-2.5%), the trend of decreasing concentration with depth indicated some accumulation in the sediment over the years. The 1.0-2.5% Corgin core 2 commonly occurs in silty-clay sediment along the centra] west coast of India 16 even in areas where there is no apparent input of anthropogenic organic matter. Hence, the extent of accumulation in the sediment of Gorai creek is small though the anthropogenic inputs have increased substantially over the past 20 y. We presume that under tropical temperatures, the excess organic loads are largely oxidised and remineralised by rich bacterial populations at the sediment-water interface apart from being consumed by benthic fauna such as polychaetes, and bivalves which are present in high numbers in the creek<sup>17</sup>. Bacterial remineralisation of organic matter is enhanced by the increase in temperature<sup>2</sup>.

 $P_{total}$  content (775-1178  $\mu g$  g<sup>-1</sup>, dry wt) also showed small but progressive accumulation in the sediment. The sediment in the region is largely derived from the lithogenic flux of soil of basaltic origin<sup>18</sup>. The basalts of the catchment areas contain  $P_{total}$  in the range (770-1500  $\mu g$  g<sup>-1</sup>)<sup>19</sup>. Similar levels prevailed in the sediment of Gorai creek.

Chlorinity of water overlying the sediment varied widely from  $6.2 \times 10^{-3}$  in August under the influence of monsoon (mid-June to mid-September), to  $21.3 \times 10^{-3}$  in early June due to excessive summer evaporation and negligible input of freshwater, in line with the

trends in creeks around Mumbai .

The chlorinity of the surficial interstitial water compared well with that of the creek water, however, below the surface, marked changes were evident (Fig. 3). Generally, the interstitial water chlorinity is sensitive to the changes in composition of the overlying water up to a certain depth decided by factors such as sediment type, porosity, diffusion rate and bioturbation<sup>14</sup>. As the core 1 was retrieved during August, after about 2 months of commencement of the monsoon, sufficient time had elapsed for low chlorinity creek water to influence the chloride content of sub-surface interstitial water through a combination of factors such as advection, diffusion and/or infiltration. This resulted in a marked positive chlorinity gradient up to a depth of 28 cm. Incidentally, this was the depth up to which porosity was relatively high (Fig. 2). Below this depth and up to 52 cm chlorinity changed only marginally (18.0 to 19.2 x 10). Although the extent of gravity induced vertical flow in deep-sea fine grained sediment is uncertain, extremely long time periods are considered necessary to cause significant changes in interstitial water composition due to the influence by overlying seawater<sup>20</sup>. The chlorinity profile in core I indicates much quicker infiltration of less saline creek water in the sediment. Assuming that the low chlorinity creek water began infiltrating with the commencement of monsoon (15 June), a rough estimate of infiltration works out to be 1.3 mm d<sup>-1</sup>. Evidently, the transport of creek water into the sediment would primarily be occurring through some other mechanism. We pre-



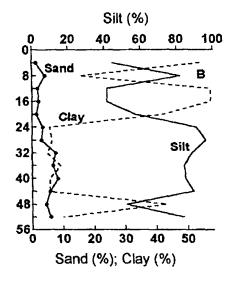


Fig. 2—Depth profiles of sediment porosity of core 4;  $C_{org}$  and  $P_{total}$  in core 2 (A); and sand, silt and clay content of core 1(B).

sume this mechanism to be bioturbation. The fine-grained sediment of creeks and bays around Mumbai sustain high biomass of macrobenthos including polychaetes, and bivalves'<sup>7</sup>. These organisms burrow into the sediment several centimeters below the bed level. Some organisms remain in their burrows and flush the burrows with the overlying seawater, thus bringing about enhanced exchange between the interstitial water and seawater<sup>14</sup>. The chlorinity profiles of cores 2 to 5 markedly differed from that of core 1. In these cores the chlorinity decreased with depth attaining minima at different levels and then systematically increased with depth. However, the segment of minimum chlorinity progressively moved downwards

from 20 cm in core 2 to 44 cm in core 5. This can be explained as - with the withdrawal of monsoon in September, the creek waters around Mumbai attain chlorinities close to that of the coastal seawater<sup>17</sup>. This high chlorinity Gorai creek water infiltrated in the sediment, progressively pushing down the monsoonal low chlorinity water trapped within the sediment. The trend indicated that the chlorinity minimum layer occurring near the base of the core 5 would migrate further downwards. Thus by the commencement of the following monsoon, the signature of the previous monsoonal chlorinity would be lost in the top 50 cm of the sediment. This explains the absence of chlorinity minimum in core 1.

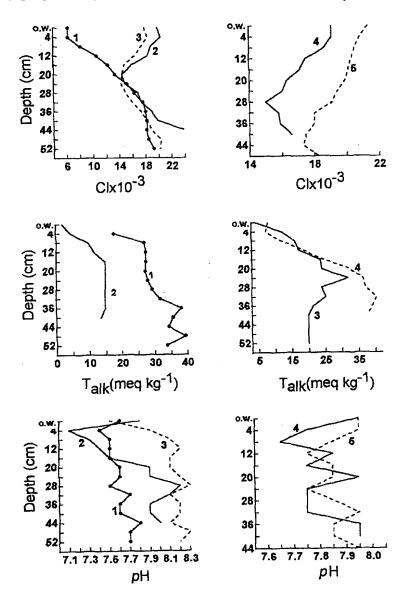


Fig. 3—Depth profiles of interstitial water chlorinity,  $T_{alk}$  and pH. Number against a profile indicates core number and o.w. represents value in creek water overlying the sediment.

The  $T_{alk}$  of the overlying water varied widely (1.9-7.9 meq kg<sup>-1</sup>) but was generally lower than that of interstitial waters of the surface segments. Talk being a sensitive indicator of microbial metabolism of sedimentary organic matter<sup>21</sup>, high T<sub>alk</sub> indicated high rate of surface microbial activity particularly in core 1 in which Talk of the interstitial water of surface sediment layer was 17.1 meq kg<sup>-1</sup>. There was a steady and systematic increase in T<sub>alk</sub> down the cores attaining high values below 32 cm in core 1 (33.6-38.2 meg kg<sup>-1</sup>) and maximum at 24 cm in core 3 (31.9 meq kg<sup>-1</sup>) and at 32 cm in core 4 (40.5 meq kg<sup>-1</sup>). The general T<sub>alk</sub> profiles resembled the variations of NH<sub>4</sub><sup>+</sup>-N concentrations (Fig. 4) with positive correlation coefficients of 0.85 (p=0.001, n=13), 0.62 (p=0.01, n=13) and 0.88 (p=0.001, n=10) between alkalinity and  $NH_4^+$ -N for cores 1, 3 and 4 though at the concentrations of NH<sub>4</sub><sup>+</sup>-N occurring in the interstitial waters of these cores (Fig. 4), its contribution to alkalinity would not be more than 2.5 meg kg<sup>-1</sup>. The occurrence of high concentrations of NO3-N (Fig. 4) throughout the core lengths rules out the possibility of sulphate reduction that can also result in high alkalinity.

The pH of the coastal seawater normally falls between 7.8 and 8.3 and is controlled<sup>22</sup> by the buffering action of  $HCO_3$ . The lower pH (7.5-7.9) of the overlying water of Gorai creek was perhaps indicative of high microbial activity in the water column. The variation of pH of interstitial water was over a wider range (7.1-8.3) though for an individual core the change down the length was not substantial (Fig. 3) in the absence of sulphate reduction.

The concentration of NO<sub>3</sub>-N was high (9-26 μmol 1<sup>-1</sup>) in the overlying water during all measurements except during June when low concentration (1 μmol 1<sup>-1</sup>) was recorded. The high NO<sub>3</sub>-N in this creek is typical of the inshore waters of Mumbai<sup>17</sup>. However, abnormally low concentration of NO<sub>3</sub>-N during June in Gorai creek, suggests denitrification at low tide (when the sample was collected). In the nearby Versova creek that receives high anthropogenic organic fluxes, complete depletion of dissolved oxygen (DO) occurs at low tides and denitrification ensues with NO<sub>3</sub>-N levels falling close to zero, just prior to the commencement of the following flood tide<sup>1</sup>.

In unpolluted coastal surface seawater, the  $NO_2$ -N is generally below 1  $\mu$ mol 1<sup>-1</sup> and is an intermediate product during the microbial oxidation of ammonia to nitrate. The concentration of  $NO_2$ -N in Gorai creek though lower than that of  $NO_3$ -N, was often abnor-

mally high. The proliferation of certain autotrophic bacteria (Nitrosomonas sp.) and inhibition of Nitrobacter sp. leads to the accumulation of NO<sub>2</sub>-N in some waters<sup>23</sup> which is not immediately oxidised to nitrate. Such accumulation of NO2-N has also been reported earlier<sup>17</sup>. The concentrations of NH<sub>4</sub><sup>+</sup>-N were also fairly high and varied widely (9-45 µmol 1<sup>-1</sup>). Molar ratio of nitrogen  $(NO_3-N + NO_2-N + NH_4^+-N)$ : Phosphorus (PO<sub>4</sub><sup>3</sup>-P) in the coastal water of Mumbai is often lower than that considered (16) for seawater on the basis of Redfield composition of plankton . The ratios for the overlying water of Gorai creek though varied widely (2.3 - 13.9), were often in the range observed for the coastal waters of Mumbai but higher than the ratios reported for Versova and Mahim creeks<sup>17</sup>. The N:P ratio of as low as 2.3 in Gorai creek suggested that a portion of the nitrogen was perhaps lost as gas during denitrification occurring around low tides.

A considerable concentration gradient  $NO_3$ -N existed between the surficial interstitial water and the overlying seawater (Fig. 4). The concentration of  $NO_3$ -N in interstitial water of the surface sediment increased from 51 µmol  $\Gamma^1$  in core 1 to 140 µmol  $\Gamma^1$  in core 5 except for a marginal decrease (83 µmol  $\Gamma^1$ ) in core 4. Marked gradient was also evident in case of  $NH_4^+$ -N and  $PO_4^{3^-}$ -P. Evidently there was sizable accumulation of the products of oxidation of organic matter, in the interstitial water as the dry season progressed.

The sedimentation rate in Gorai creek is not known. However, in the creeks around Mumbai sediments accumulate<sup>25</sup> rapidly at a rate of 0.4-1.9 cm y<sup>-1</sup>. The rate of sedimentation in Gorai creek could be of the same order. A peak in NO<sub>3</sub>-N concentration was evident in 0-4 cm sections in all cores (Fig. 4) immediately below which the concentrations decreased substantially. Hence, the oxic zone in these sediments was confined, at the most, to the top 4 cm of the sediment.

The nitrogenous products of aerobic oxidation of organic matter are mainly nitrate and nitrite since ammonia produced during heterotrophic breakdown is biochemically oxidised to nitrate via nitrite<sup>26,27</sup>. However, the presence of very high levels of NH<sub>4</sub><sup>+</sup>-N (195-796 µmol  $\Gamma^1$ ) in interstitial waters of even 0-4 cm segment of all cores indicated that the ammonia produced during heterotrophic breakdown of organic matter was not immediately oxidised and accumulated in the interstitial water prior to its transport pre-

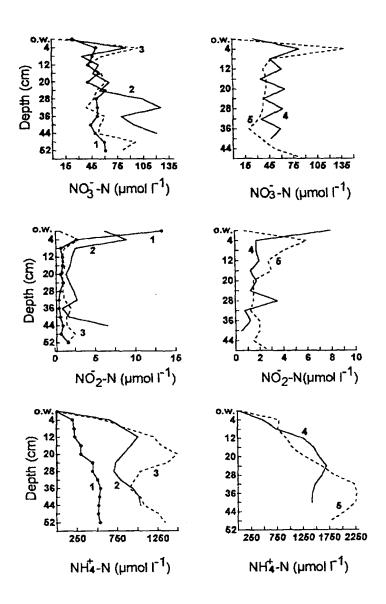


Fig. 4—Depth profiles of interstitial water  $NO_3$ -N,  $NO_2$ -N and  $NH_4^+$ -N. Number against a profile indicates core number and o.w. represents value in creek water overlying the sediment.

dominantly to the sediment below, along with chlorinity. The nitrate produced via oxidation of ammonia when transported downwards was partially consumed for the oxidation of organic matter in the absence of DO via biologically catalysed denitrification reaction<sup>28</sup>.

The NO<sub>3</sub>-N profiles were anomalous in one respect: all cores except core 4, showed relative increase in concentration below a certain depth. Under normal steady state diagenetic conditions, denitrification should produce an exponentially decreasing NO<sub>3</sub>-N profile <sup>14,26</sup>. Because of peculiar NO<sub>3</sub>-N profile in present cores, we suspected a nonsteady state condition

in these sediments which could result from either of the two following factors - the sediment in this zone could have been buried at a time when the bottom water NO<sub>3</sub>-N concentrations were abnormally high or else, the nitrate in this zone was consumed less rapidly than above, due to the differences in organic matter and/or microbial populations. The former possibility was less likely, since even if we assumed a high sedimentation rate of 1.5 cm y<sup>-1</sup>, sediment below 44 cm depth where high concentration of NO<sub>3</sub>-N were observed, was probably buried about 30 y back. The urbanisation of coastal land around the creek is fairly recent (15-20 y) and the water body was nearly free from wastewater discharges in the past. Hence.

the then existing NO<sub>3</sub>-N levels in water would be much lower.

The modeling of NO<sub>3</sub>-N under steady state and nonsteady state conditions indicates that the diffusion would eliminate large transient NO<sub>3</sub>-N pulses on a time scale of days<sup>26</sup> in rapidly accumulating (sedimentation rate of 0.5 to 1.0 cm v<sup>-1</sup>) sediments. The other possibility is that there could be a NO<sub>3</sub>-N source operating in these sediments to balance diffusional losses. Such a source has to be biochemical in nature since NO<sub>3</sub>-N is not present in any marine mineral phases<sup>27</sup>. An intermediate zone of high NO<sub>3</sub>-N at 20-30 cm depth in the interstitial water of sediments from Puget Sound<sup>27</sup> (USA) has been attributed to nitrification with DO being supplied through irrigation by burrowing benthic organisms. Although clayey-silt sediment of Mumbai was rich in macrobenthos particularly polychaetes<sup>17</sup>, organisms which could have burrows extending below 40 cm have not been reported and are not expected to occur<sup>17</sup>. Hence, it is unlikely that the high NO<sub>3</sub>-N levels in lower section could result from nitrification. Moreover, the chlorinity profile did not support transport of creek water in the cores below 40 cm directly in which case the chlorinities of the overlying water and interstitial waters below 40 cm would be comparable. We, therefore, feel that the NO<sub>3</sub>-N transported to the lower section, is consumed slowly perhaps due to the lower content of oxidisable organic matter in the bottom section.

The NO<sub>2</sub>-N concentration in the interstitial water throughout the length in all cores was less than 9.1 µmol I<sup>-1</sup>. Typically, the 0-4 cm layer sustained highest concentration (Fig. 4) because of its formation during the aerobic oxidation of ammonia. Further, there was no evidence for formation of NO<sub>2</sub>-N in the nitrate reduction zone in present cores. From nitrification rates and fluxes of NO<sub>3</sub>-N, NO<sub>2</sub>-N and NH<sub>4</sub><sup>+</sup>-N in Tamar estuary, Law *et al.*<sup>28</sup> concluded that nitrification was the source of NO<sub>2</sub>-N in sediments.

Except in core 1 in which the concentration of NH<sub>4</sub><sup>+</sup>-N increased monotonously with depth, in all other cores an intermediate maximum prevailed (Fig. 4) that gradually shifted downwards from 8-12 cm in core 2 to 32-36 cm in core 5 with in-between positions in cores 3 and 4. These however, did not coincide with the minimum in chlorinity profiles and their position was markedly above the chlorinity minimum in all cores. This is expected since unlike halides, which do not undergo adsorption-desorption mecha-

nism with sediment particles, ammonia is adsorbed by clay particles<sup>29</sup> and therefore its residence time at a grain site is prolonged during downward transport. A continuous build-up of  $\mathrm{NH_4}^+$ -N in interstitial waters over the dry season unlike other nutrients was evident with an increasing trend from 195-539  $\mu$ mol 1<sup>-1</sup> in core 1 to 771-2272  $\mu$ mol 1<sup>-1</sup> in core 5.

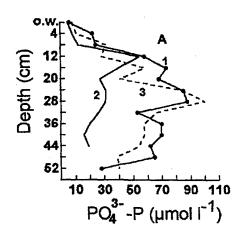
The levels of  $PO_4^{3-}$ -P in the creek water were high (5-15 µmol 1<sup>-1</sup>) and typical of creek systems of Mumbai. These levels are considerably higher than the open shore waters of Mumbai (1-4 µmol 1<sup>-1</sup>)<sup>17</sup>. Similar to the concentrations of other nutrients, the levels of  $PO_4^{3-}$ -P were high (8-28 µmol 1<sup>-1</sup>) in interstitial waters of 0-4 cm sections (Fig. 5). The depth profiles of  $PO_4^{3-}$ -P are also indicative of downward transport though the maxima are not as clearly defined as in the case of chlorinity and  $NH_4^+$ -N.

The molar ratios of N  $(NO_3-N + NO_2-N + NH_4^+$ N): P  $(PO_4^{3-}-P)$  were markedly high (20-93) in 0-4 cm sections as compared to the ratios associated with the creek water suggesting the removal of PO<sub>4</sub><sup>3</sup>-P from the interstitial water. The sediment of Gorai creek having been derived from basaltic terrain 18 is rich in iron. Ferric ion can interact<sup>14</sup> chemically with orthophosphate to form insoluble phosphate-iron (III) complexes FePO<sub>4.2</sub>H<sub>2</sub>O. The phosphate from interwaters can also form hydroxyapatite [Ca<sub>5</sub>OH(PO<sub>4</sub>)3] which is insoluble under oxic conditions<sup>14</sup>. Below 4 cm depth, the magnitude of the N:P molar ratio was largely controlled by the concentrations of NO<sub>3</sub>-N and PO<sub>4</sub><sup>3</sup>-P. The high PO<sub>4</sub><sup>3</sup>-P concentrations below 4 cm depth would occur due to downward transport as discussed earlier and may not be a consequence of release from sediment since reduction of iron was unlikely in the presence of high concentration of NO<sub>3</sub>-N.

The fluxes of nutrients were calculated from Fick's first law as described by Berner<sup>14</sup>

$$J = \phi D_s (C/x)_{x=0}$$

where, J = the mass flux of interstitial water constituent being considered,  $D_s$  = whole-sediment diffusion coefficient of the constituent, C = the concentration of interstitial water constituent being considered,  $\phi$  = the porosity of surface sediment, x = the length of coordinate, measured positively into the sediment with origin at the interface, and ( $C/x)_{x=0}$  = the concentration gradient across the sediment-water interface. Bulk sediment diffusion coefficients ( $D_s$ ) were



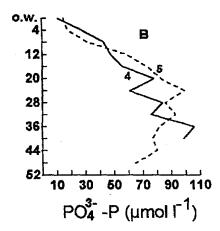


Fig. 5—Depth profiles of interstitial water  $PO_4^{3-}$ -P. Number against a profile indicates core number and o.w. represents value in creek water overlying the sediment. [A = cores 1-3, B = cores 4,5]

Table 1—Fluxes of nutrients ( $\mu$ mol m<sup>-2</sup> d<sup>-1</sup> ) across the sediment-water interface

Core	$NO_3$ -N	$NO_2$ -N	$\mathrm{NH_4}^+\mathrm{-N}$	PO <sub>4</sub> <sup>3-</sup> -P
1	-54	21	-377	-10
2	-133	-5	-1240	-2
3	-177	-5	-1159	-2
4	-111	12	-934	-11
5	-270	10	-1548	-2

calculated from seawater values' following the procedure of Ullman & Aller<sup>31</sup> by using equation

$$D_s = D_0/\phi F$$

Since in present cores surface porosity was > 0.7, the value of m in the empirical relation  $F=1/\phi^m$  (F is the electrical resistivity factor and m is an appropriate exponent) was considered<sup>32</sup> as 3. The result of calculations given in Table 1 indicated that the fluxes of all nutrients were oriented towards the water column except for nitrite which was into the sediment in some instances. It is also evident that the fluxes of nitrate and ammonia generally increased from core 1 to core 5 with a definite decrease in core 4. Such an increase can be due to increase in temperature which, not only accelerates the microbial reactions but also enhances the rate of molecular diffusion<sup>14</sup>. This was further supported by low flux of  $NH_4^+$ -N (-934  $\mu$ mol m<sup>-2</sup>d<sup>-1</sup>) as well as NO<sub>3</sub>-N (-111 µmol m<sup>-2</sup>d<sup>-1</sup>) in core 4 retrieved during January when the temperature (winter) was expected to be relatively low.

Samlping interval in present cores being 4 cm, the processes occurring at the sediment-water interface could not be resolved. Hence, the values in Table 1 should be considered only as suggestive of partial transport of nutrients to the overlying water in gross terms.

From the foregoing discussion it appears that the nutrients released in the surficial interstitial water were partly transported to the overlying water while a significant fraction migrated into the sediment along with chlorinity.

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